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(54) HEAT-RESISTING ADHESIVE AGENT FILM FOR PRINTED BOARD AND ITS MANUFACTURING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a heat-resisting adhesive agent film, capable of thermocompression bonding at a low temperature without damaging superior heat-resisting property and electrical characteristics which are proper to polyimide, and to provide its manufacturing method and applying method.
SOLUTION: This heat-resisting adhesive agent film for a printed board is composed of polyimide resin of 70-99 wt.% which has silicon unit, epoxy resin of 1-30 wt.% whose epoxy equivalent is at most 500, and epoxy resin hardener. The film is inserted in a part between members to be bonded, and is used by thermocompression bonding under the conditions where the pressure is 1-100 kg/cm2 and the temperature is 20-250°C.

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of a heat-resistant adhesive film for printed circuit boards drying it after the surface coats a solution which dissolved in an organic solvent of a constituent which consists of 70 to 99 % of the weight of polyimide resin and 1 to 30 % of the weight of epoxy resins which have a silicon unit on a substrate by which exfoliation processing was carried out.
[Claim 2]A heat-resistant adhesive film for printed circuit boards which consists of 70 to 99 % of the weight of polyimide resin which has a silicon unit, 1 to 30 % of the weight of epoxy resins, and 1 to 15 % of the weight of epoxy resin hardeners.
[Claim 3]A heat-resistant adhesive film for printed circuit boards which consists of 70 to 99 % of the weight of polyimide resin which has a silicon unit, 1 to 30 % of the weight of epoxy resins, and 0 to 15 % of the weight of epoxy resin hardeners is inserted between bonded objects, The directions for a heat-resistant adhesive film for printed circuit boards bonding by thermo-compression on the pressure 1 - 100 kg/cm^2, and conditions with a temperature of 20-250 **.

[Translation done.]

DETAILED DESCRIPTION

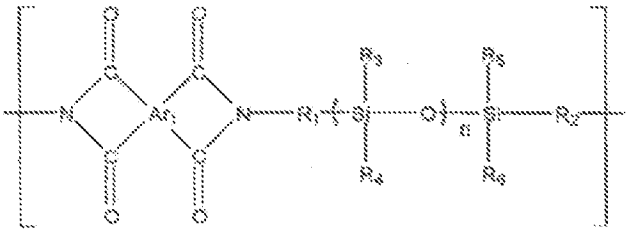
[Detailed Description of the Invention]
[0001]
[Field of the Invention]Especially this invention relates to the new heat-resistant adhesive film for printed circuit boards which becomes an organic solvent which has a silicon unit from meltable polyimide resin and epoxy resin about the heat-resistant adhesive film for printed circuit boards.
[0002]
[Description of the Prior Art]What pasted together a substrate or a polyimide film, a polyethylene terephthalate film, etc. which consist of paper-phenol resin and a glass fiber-epoxy resin conventionally, and the metallic foil as a printed-circuit board is used.
[0003]In the printed wired board used in the field of the electrical and electric equipment and a precision mechanical equipment, a wiring occupation area becomes small and, for this reason, the demand of multilayer interconnection boards is increasingly higher in recent years. A printed-circuit board is laminated, a multilayer interconnection board is created or various adhesives or adhesive films are used in the process of composite-izing circuit material of a different kind.
[0004]As such adhesives, the prepreg-like adhesives which impregnated textiles, such as glass fiber, with an epoxy system or bismaleimide system resin are known. However, these have insufficient flexibility and there were problems, such as being inferior to dimensional stability. Conventionally Acrylonitrile-butadiene rubber/phenol resin, Adhesives, such as phenol resin/butyral resin, acrylonitrile-butadiene rubber/epoxy resin, are proposed (JP,4-29393,A, JP,4-36366,A, JP,4-41581,A). However, chemical resistance and heat resistance were not enough, these adhesives had large heat deterioration, and their moisture absorption solder heat resistance was insufficient, and they were not enough in respect of processability, such as generating of the smear at the time of drill drilling processing for through hole formation.

[0005]The polyimide system adhesives which were excellent in heat resistance in recent years are also proposed. For example, the thermoplastic polyimide adhesive currently indicated by USP4,543,295 is known. However, such polyimide pasted up substrates, such as copper or a polyimide film, and since it needed the thermo-compression-bonding temperature of not less than 250 ** in order to obtain satisfying adhesive strength, it had a difficulty in respect of practicality.
[0006]In order to perform thermo compression bonding at low temperature, the adhesives using the polyimide which uses a diaminopolysiloxane and aromatic tetracarboxylic acid as a raw material are proposed (JP,4-23879,A). However, in such a polyimide simple substance, there was a fault that adhesive strength was not enough and was inferior to reliability.
[0007]As polyimide system adhesives excellent in adhesive strength, the film adhesive which becomes JP,52-91082,A from polyamidoimide and an epoxy resin as adhesives for manufacture of the copper-clad film for flexible printed wiring boards is indicated. However, when it uses for adhesion of the rugged surfaces in which circuits, such as multilayer printed wiring board manufacture, were formed, such a film does not have the enough restoration nature to a circuit face, and cannot fully obtain heat resistance to a solder bath.
[0008]For this reason, as the adhesives for multilayer PURINDO boards, and adhesives for cover lay films, low-temperature sticking by pressure of 250 ** or less is possible, and the material which was moreover excellent in adhesive strength, chemical resistance, heat resistance, moisture absorption solder heat resistance, the dimensional stability at the time of wiring processing, etc. has come to be called for.
[0009]
[Problem(s) to be Solved by the Invention]This inventions are thermo-compression-bonding conditions 250 ** or less, and an object of this inventions is to provide the heat-resistant adhesive film for printed circuit boards excellent in heat resistance, moisture absorption solder heat resistance, processability, etc.
[0010]
[Means for Solving the Problem]Namely, a solution which dissolved this invention in an organic solvent of a constituent which consists of 70 to 99 % of the weight of polyimide resin and 1 to 30 % of the weight of epoxy resins which have a silicon unit, After the surface coats on a substrate by which exfoliation processing was carried out, it is a manufacturing method of a heat-resistant adhesive film for printed circuit boards to dry. What consists of 70 to 99 % of the weight of polyimide resin which has a silicon unit, 1 to 30 % of the weight of epoxy resins, and 1 to 15 % of the weight of epoxy resin hardeners as said heat-resistant adhesive film for printed circuit boards is mentioned.
[0011]If mixing with polyimide resin is possible for an epoxy resin used in this invention, limitation in particular will not be carried out, but a weight per epoxy equivalent is a liquefied or

powdered epoxy resin which is 500 or less range preferably. If a weight per epoxy equivalent exceeds 500, adhesive strength and heat resistance will fall. As an example of such an epoxy resin, bisphenol A, the bisphenol F. Phenols, such as the bisphenol S, a fluorene bisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, and resorcinol, Or tris-(4-hydroxyphenyl) methane, 1,1,2,2-tetrakis (4-hydroxyphenyl) ethane, There is a glycidyl ether ghost derived from halogenated bisphenols, such as phenols more than trivalent [, such as phenol novolac and o-cresolnovolak,] or tetrabromobisphenol A. These epoxy resins can mix and use one sort or two sorts or more.

[0012]In this invention, it is desirable for a film moldability to use good solvent solubility polyimide as polyimide resin which has a silicon unit. As an example suitably used as polyimide which has solvent solubility, it is a following general formula (1).

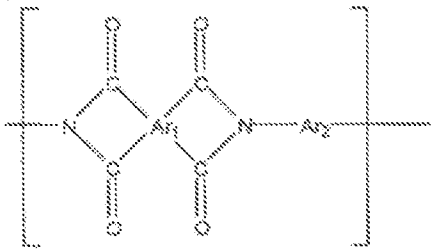
[Formula 1]



(1)

(However, Ar_1 showing a tetravalent aromatic group, R_1 and R_2 showing a divalent hydrocarbon group, R_3 - R_6 showing the hydrocarbon group of the carbon number 1 - 6 values, and n showing the integer of 1-20), and a following general formula (2)

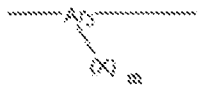
[Formula 2]



(2)

At least 1-mol % is a following general formula (3) among Ar2 [in / preferably / it has a repeating unit expressed with (however, Ar_1 shows a tetravalent aromatic group and Ar_2 shows a divalent aromatic group), and / the above-mentioned general formula (2)].

[Formula 3]



(3)

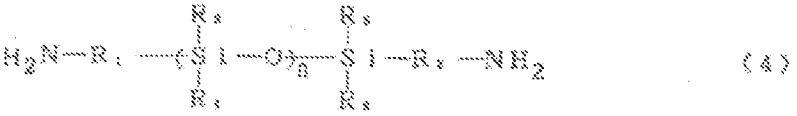
It is polyimide resin which has an aromatic group expressed with (however, Ar_3 shows a trivalent or tetravalent aromatic group, X shows a hydroxyl group, an amino group, or a carboxyl group, and m shows 1 or 2).

[0013]The polyimide resin which has a repeating unit expressed with the above-mentioned general formula (1) and (2) is obtained by making a diamino siloxane and aromatic diamine, and tetracarboxylic dianhydride react.

[0014]As an example of tetracarboxylic dianhydride, preferably 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and 2,2',2,3'-benzophenone tetracarboxylic dianhydride are mentioned. Otherwise, as a part of tetracarboxylic dianhydride ingredient, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 2,3,3',4'-biphenyl tetracarboxylic dianhydride, pyromellitic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 3,4,9,10-perylene tetracarboxylic dianhydride, 3,3,6,7-anthracene tetracarboxylic dianhydride, 1,2,7,8-phenanthrene tetracarboxylic dianhydride, 4,4'-(hexafluoro iso PIRIDEN) phthalic acid dianhydride, etc. can also be used together.

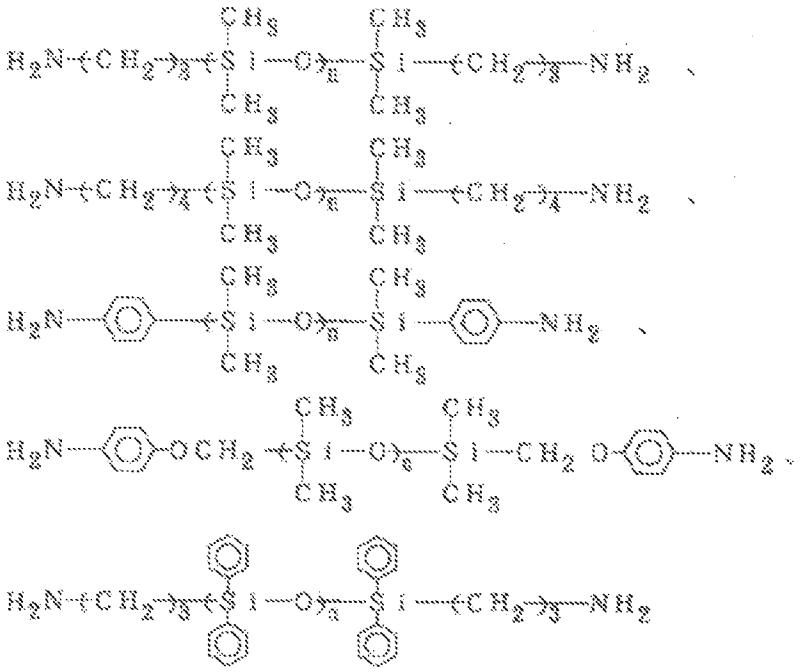
[0015]As a diamino siloxane, it is a following general formula (4).

[Formula 4]



(4)

The diamino siloxane expressed with (however, R_1 and R_2 show a divalent hydrocarbon group, R_3 - R_8 show the hydrocarbon group of the carbon numbers 1-6, and n shows the integer of 1-20) is used. As an example, it is preferably. [Formula 5]



** is mentioned. It is the range of 1-20 preferably [n / an average of / of these diamino siloxanes / more than], and is the range of 5-15 more preferably. Since the restoration nature of a heat-resistant adhesive film will fall if less than this range, it is not desirable. Since an adhesive property will fall if more than this range, it is not desirable. By introducing a silicon unit into polyimide resin using these diamino siloxanes, the mobility at the time of heat crimping can be given to the heat-resistant adhesive film of this invention, and the restoration nature to a plated printed circuit side can be raised.

[0016]As an example of aromatic diamine, m-phenylenediamine, P-phenylene diamine, 4,4'-diaminodiphenylpropane, A 4,4'-diaminodiphenylmethane, benzidine, 4, and 4'-diamino diphenyl sulfide, Although 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 4,4'-diamino-p-terphenyl, etc. are mentioned, In order to raise fusibility over an organic solvent 2,2-bis(3-aminophenoxy phenyl) propane, 2,2-bis(4-aminophenoxy phenyl)propane, a 3,3-bis(3-aminophenoxy phenyl)sulfone, A 4,4-bis(3-aminophenoxy phenyl)sulfone, a 3,3-bis(4-aminophenoxy phenyl)sulfone, A 4,4-bis (4-aminophenoxy phenyl)sulfone, 2,2-bis(3-aminophenoxy phenyl)hexafluoropropane, 2,2-bis (4-aminophenoxy phenyl)hexafluoropropane, 1,4-bis(4-aminophenoxy)benzene, It is preferred to use diamine which has three or more aromatic rings, 1,3-bis(4-aminophenoxy)benzene, 4,4-(p-phenylenediisopropylidene) screw aniline, 4,4-(m-phenylenediisopropylidene) screw aniline, etc.

[0017]It is more preferred to blend diamine which has an aromatic group expressed with the above-mentioned general formula (3) which has an epoxy resin and a functional group which has reactivity in a part of above-mentioned aromatic diamine. As aromatic diamine which has a

reactive functional group to such an epoxy resin, 2,5-diaminophenol, 3,5-diaminophenol, 4,4'-(3,3'-dihydroxy) diaminobiphenyl, 4,4'-(2,2'-dihydroxy) diaminobiphenyl, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, Although 3,3',4,4'-biphenyltetramine, 3,3',4,4'-tetraminodiphenyl ether, 4,4'-(3,3'-dicarboxy) diphenylamine, and 3,3'-dicarboxy-4,4'-diaminodiphenyl ether etc. are mentioned, They are 4,4'-(3,3'-dihydroxy) diphenylamine and 4,4'-(2,2'-dihydroxy) diphenylamine especially preferably. Since it reacts to an epoxy resin at the time of heat crimping and the structure of cross linkage is formed by using these aromatic diamine, adhesive strength of heat-resistant adhesives of this invention and chemical resistance can be raised further. aromatic diamine which has a reactive functional group to the above-mentioned epoxy resin -- all the aromatic diamine -- at least -- more than 1 mol % -- using is 1-10-mol% of the range desirable especially preferably.

[0018]Polyimide resin can manufacture polyimide resin which has a repeating unit expressed with said general formula (1) and (2) by [which made tetracarboxylic dianhydride react to the above-mentioned diamino siloxane and aromatic diamine in a solvent, and generated precursor resin] carrying out a back heating ring closure. It is preferred that ranges of percentage of a repeating unit expressed with the general formula (1) and (2) at this time are (1)/(2) =50 / 50 - 10/90. An effect of this invention is not acquired out of this range.

[0019]A blending ratio of polyimide resin and an epoxy resin which have the above-mentioned silicon unit is the range of 70 to 99 % of the weight of polyimide resin, and 1 to 30 % of the weight of epoxy resins. Heat resistance and an adhesive property can be raised further, without reducing the original characteristic of polyimide resin by blending in this range.

[0020]An epoxy resin hardener can also be blended with everything but the above-mentioned polyimide resin and an epoxy resin for the purpose of promotion of hardening as occasion demands. As an example of an epoxy resin hardener, acid anhydrides, such as amines, such as phenols, such as phenol novolac, o-cresolnovolak, and phenol resol, and diethylenetriamine, pyromellitic dianhydride, and phthalic anhydride, are mentioned.

[0021]As for a blending ratio of each ingredient at the time of blending an epoxy resin hardener, it is preferred that it is the range of 70 to 98 % of the weight of polyimide resin, 1 to 15 % of the weight of epoxy resins, and 1 to 15 % of the weight of epoxy resin hardeners.

[0022]In this invention, a hardening accelerator more publicly known than before, a coupling agent, a bulking agent, paints, etc. other than each above-mentioned ingredient may be blended suitably if needed.

[0023]Although heat-resistant adhesives of this invention which consists of each above-mentioned ingredient are fabricated and used for film state, it is possible to film-ize using a publicly known method conventionally. As an example of a suitable forming process, resin which consists of an ingredient of polyimide resin, an epoxy resin, and others is dissolved in a solvent, It can be considered as a heat-resistant adhesive film for printed circuit boards of this

invention by drying and exfoliating from a substrate, after the surface coats an obtained resin solution by a publicly known method conventionally on substrates, such as a metallic foil by which exfoliation processing was carried out, polyester film, and a polyimide film.
[0024]As a thing typical as a solvent used by the above-mentioned film forming cycle, N,N-dimethylformamide, a N,N-diethylformamide, N,N-dimethylacetamide, A N,N-diethylacetamide, a N,N-dimethyl methoxy acetamide, Amide system solvents, such as dimethyl sulfoxide and N-methyl-2-pyrrolidone, A tetrahydrofuran, diethylene glycol dimethyl ether, diethylene-glycol diethylether, Dioxane, gamma-butyrolactone, a xylenol, chlorophenol, Ether, such as phenol, methyl cellosolve, ethylcellosolve, methyl-cellosolve acetate, ethylcellosolve acetate, toluene, xylene, and methyl ethyl ketone, ester, and alcoholic solvent can be mentioned. Even if it uses a solvent used at the time of said polyimide resin manufacture as it is as a solvent at the time of film shaping, it does not interfere at all.
[0025]As the suitable directions for a heat-resistant adhesive film of this invention, For example, among bonded objects, such as a flexible printed circuit board, a glass fiber-epoxy wiring board, a paper-phenol wiring board, metal, and a resin base material, Insert a heat-resistant adhesive film of this invention, and it bonds by thermo-compression on condition of temperature of 20-250 **, the pressure 1 - 100 kg/cm^2, A method of making a glue line form between bonded objects is mentioned by carrying out predetermined time heat treatment at temperature of further 50-250 ** preferably, and stiffening an epoxy resin thoroughly.
[0026]
[Embodiment of the Invention]Since the polyimide which has a silicon unit used for the film for printed circuit boards of this invention is solvent solubility, while composite-izing with an epoxy resin is possible for it, since it has a silicon unit, mobility good at the time of thermo compression bonding is shown, and it has restoration nature and adhesion outstanding to the bonded object. By using the aromatic diamine which has an epoxy resin and reactivity, a bridge is constructed with an epoxy resin and it has the feature that the glue line excellent also in intensity and heat resistance can be formed. Since the glass transition point is low, compared with the conventional polyimide system adhesives, it can paste up at low temperature far.
[0027]
[Example]An example is shown below and this invention is explained to it in more detail. The cable address used by this example shows the following compounds.
ODPA:. 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride DSDA:3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride BTDA:3,3',4,4'-benzophenone tetracarboxylic dianhydride BPDA :. 3,3',4,4'-biphenyl tetracarboxylic dianhydride BAPP:2,2'-bis(4-aminophenoxy phenyl)propane BAPS:bis(4-aminophenoxy phenyl)sulfone mBAPS : Bis(3-aminophenoxy phenyl)sulfone BisAM:. A 1,3-screw. (Aminoisopropyl) Benzene DABP:. 3,3'-diaminobenzophenone HAB:4, 4'-

. (3,3'-dihydroxy) Diaminobiphenyl oDAP:. A 2,5-diaminophenol HFP:2,2'-screw. diamino Siloxane PSX-D: (3-amino-4 hydroxyphenyl) hexafluoropropane PSX-A: -- diamino siloxane PSX-B: of the average molecular weight 740 -- diamino siloxane PSX-C: of the average molecular weight 1000 -- the average molecular weight 1240. The diamino siloxane DGEBA of the average molecular weight 2000 : Bisphenol type A epoxy resin oCNB:o-cresolnovolak. Mold Epoxy-resin BCNB: Bromo cresol novolak type epoxy resin PNB: Phenol novolak resin

[0028]To the separable flask of 11 l. of examples, ODPA37.14g (0.11 mol), 200g of N-methyl-2-pyrrolidone and the diethylene glycol dimethyl ether 200g are inserted in, At a room temperature, use a dropping funnel for the well mixed next, and PSX-A 31.56g (n = 8.4 or 0.04 mol) is dropped at it. It ice-cooled under stirring of this reaction solution, o-DAP 1.52g (0.01 mol), BAPP30.25g (0.07 mol), and HAB1.04g (0.005 mol) were added, it stirred at the room temperature for 2 hours, and the polyamic acid solution was obtained. Temperature up was carried out to 190 **, it heated, this polyamic acid solution was stirred for 20 hours, and the polyimide solution of logarithmic viscosity 0.9 dl/g was obtained.

[0029]Next, mixed bisphenol A type epoxy resin (product [made from Oil recovery Shell Epoxy], Epicoat 828) 25 weight section, it was made to stir at a room temperature to solid content 75 weight section of the obtained polyimide solution for 2 hours, and the adhesive resin solution was prepared. This resin solution was applied on the glass plate, and it dried, and it film-ized and was considered as the heat-resistant adhesive film. The 5% weight loss temperature under 120 ** and a nitrogen atmosphere was 450 ** the glass transition point of this film. Tensile strength, specific inductive capacity, and volume resistance were measured based on JIS C2330, respectively about this film. A result is shown in Table 2.

[0030]thus, the obtained heat-resistant adhesive film -- the polyimide film (the Kaneka CORP. make.) of two sheets When it inserted between APIKARU and the sticking-by-pressure examination was done under the conditions of 25 kg/cm^2 for 200 ** and 60 minutes, the adhesive strength by a 180-degree peel test was 2.6 kg/cm. It was 1.8 kg/cm, when it bonded by thermo-compression on ****** and the same conditions between the oxidized copper foil of two sheets similarly and the adhesive strength by a 180-degree peel test was measured. After pasting up copper foil and being immersed for 30 seconds during a 300 ** solder bath, the adhesion state was observed, but it swelled, and defects, such as peeling, were not observed but showed good solder heat resistance.

[0031]The film was prepared by the presentation shown in Table 1 like Example 1 with the presentation shown in the two to example 10 table 1, and the various characteristics were measured. A result is shown in Table 2.

[0032]The film was prepared by the presentation shown in Table 1 like one to comparative example 5 example, and the various characteristics were measured. A result is shown in Table 2.

[0033]

[Table 1]

		ポリイミド樹脂（重量%）			エポキシ樹脂（wt%）	ゴム粒子樹脂変成剤（wt%）
		芳香族テトラカルボン酸（モル）	芳香族ジアミン（モル）	ジアミノシロキサン（モル）		
実施例	1	75			DGEBA 25	—
		ODPA 0.11	BAPP 0.07	BAB 0.005	PSX-A0.035	
	2	80			eCNB 20	—
		ODPA 0.11	BAPP 0.07	BAB 0.005	PSX-A0.035	
	3	80			eCNB 20	—
		ODPA 0.11	BAPS 0.06	BAB 0.003	PSX-A0.047	
	4	70			eCNB 20	PNB 10
		DSDA 0.12	BAPP 0.07	BAB 0.004	PSX-A0.036	
	5	80			BCNB 20	—
		DSDA 0.11	BAPS 0.06	cDAPO 0.005	PSX-C0.045	
	6	80			BCNB 20	—
		DSDA 0.13	mBAPS 0.06	HFP 0.004	PSX-D0.046	
	7	80			eCNB 20	—
		DSDA 0.11	BisAM 0.07	BAB 0.005	PSX-A0.035	
	8	75			eCNB 25	—
		BPDA 0.11	BisAM 0.07	BAB 0.005	PSX-A0.035	
	9	75			DGEBA 25	—
		BTDA 0.12	mBAPS 0.06	BAB 0.005	PSX-A0.035	
	10	70			eCNB 30	PNB 10
		ODPA 0.11	BAPP 0.07	BAB 0.005	PSX-A0.035	
比較例	1	100			—	—
		BTDA 0.10	DABP 0.10	—	—	
	2	100			—	—
		ODPA 0.11	BAPP 0.07	—	PSX-A0.040	
	3	95			DGEBA 5	—
		DSDA 0.11	BAPP 0.06	—	PSX-A0.030	
	4	100			—	—
		DSDA 0.11	BAPP 0.10	BAB 0.01	—	
	5	95			DGEBA 5	—
		DSDA 0.11	BAPP 0.10	BAB 0.01	—	

[0034]

[Table 2]

	ガラス転移温度	熱分解温度	引張強度	比誘電率	吸湿率	接着強度1	接着強度2	接着強度3	はんだ耐熱性1	はんだ耐熱性2
実施例	(℃)	(℃)	kg/cm²		x10⁻⁴ g/cm	kg/cm			(℃)	
1	120	400	7.5	3.1	2	1.8	1.3	2.6	>300	300
2	125	410	7.4	2.9	1	1.5	1.0	2.5	>300	290
3	145	430	6.0	3.0	2	1.8	1.2	2.3	>300	300
4	140	445	7.6	2.9	1	1.8	1.1	2.4	>300	300
5	165	410	6.8	3.0	2	1.9	1.3	2.6	>300	290
6	170	420	5.7	3.1	2	1.8	1.2	2.4	>300	300
7	130	410	7.5	2.9	2	1.6	1.2	2.2	>300	300
8	160	430	7.1	3.0	2	1.8	1.1	2.0	>300	290
9	150	420	6.7	3.1	2	1.6	1.1	2.0	>300	290
10	145	435	7.0	3.2	2	1.9	1.3	2.5	>300	300
比較例										
1	250	520	14.0	3.4	2	0.4	0.1	0.3	260	240
2	130	460	7.5	3.0	1	0.5	0.1	0.3	270	250
3	140	450	6.5	3.1	2	0.7	0.3	0.4	260	240
4	170	470	13.3	3.2	2	0.6	0.3	0.4	240	220
5	165	460	13.0	3.2	2	1.7	0.1	0.5	250	230

[0035]In Table 2, the adhesive strength 1 is the 180-degree peel strength to oxidation treatment copper, the adhesive strength 2 is the 180-degree peel strength to vitriolization

copper, and the adhesive strength 3 is the 180-degree peel strength to a polyimide film. The solder heat resistance 1 is an inspection about a blister, peeling, and appearance after 30-second immersion at a solder bath, and the solder heat resistance 2 inspects a blister, peeling, and appearance after 30-second immersion to a solder bath after 40 **, 90%RH, and 24-hour moisture absorption.

[0036]2 sets of flexible printed circuit boards by which the circuit was formed in both sides of example 11 polyimide film with copper are prepared, After inserting the heat-resistant adhesive film obtained in Example 1 in the meantime and bonding by thermo-compression on condition of for the temperature of 200 **, pressure 25 kg/cm^2, and 60 minutes, the through hole was formed and the multilayer printed wiring board was manufactured. There is also no generating of a smear etc. in the case of through hole formation, and the good through hole was obtained. Although this multilayer printed wiring board was immersed in a 300 ** solder bath for 30 seconds, it swelled and defects, such as peeling, were not observed.

[0037]The multilayer printed wiring board was manufactured like example 12 Example 8 using the heat-resistant adhesive film obtained in Example 10. There is also no generating of a smear etc. in the case of through hole formation, and the good through hole was obtained. Although this multilayer printed wiring board was immersed in a 300 ** solder bath for 30 seconds, it swelled and defects, such as peeling, were not observed.

[0038]

[Effect of the Invention]Compared with the conventional polyimide system adhesives, thermo compression bonding of the heat-resistant binder film for printed circuit boards of this invention at low temperature is attained, without spoiling the original outstanding heat resistance of polyimide, and an electrical property. Therefore, the heat-resistant binder film for printed circuit boards by this invention can be used conveniently for the adhesives for multilayer printed boards, the adhesives for compound circuit boards, the adhesives for cover lay films, etc.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]Especially this invention relates to the new heat-resistant adhesive film for printed circuit boards which becomes an organic solvent which has a silicon unit from meltable polyimide resin and epoxy resin about the heat-resistant adhesive film for printed circuit boards.

[Translation done.]

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PRIOR ART

[Description of the Prior Art]What pasted together a substrate or a polyimide film, a polyethylene terephthalate film, etc. which consist of paper-phenol resin and a glass fiber-epoxy resin conventionally, and the metallic foil as a printed-circuit board is used.
[0003]In the printed wired board used in the field of the electrical and electric equipment and a precision mechanical equipment, a wiring occupation area becomes small and, for this reason, the demand of multilayer interconnection boards is increasingly higher in recent years. A printed-circuit board is laminated, a multilayer interconnection board is created or various adhesives or adhesive films are used in the process of composite-izing circuit material of a different kind.
[0004]As such adhesives, the prepreg-like adhesives which impregnated textiles, such as glass fiber, with an epoxy system or bismaleimide system resin are known. However, these have insufficient flexibility and there were problems, such as being inferior to dimensional stability. Conventionally Acrylonitrile-butadiene rubber/phenol resin, Adhesives, such as phenol resin/butyral resin, acrylonitrile-butadiene rubber/epoxy resin, are proposed (JP,4-29393,A, JP,4-36366,A, JP,4-41581,A). However, chemical resistance and heat resistance were not enough, these adhesives had large heat deterioration, and their moisture absorption solder heat resistance was insufficient, and they were not enough in respect of processability, such as generating of the smear at the time of drill drilling processing for through hole formation.
[0005]The polyimide system adhesives which were excellent in heat resistance in recent years are also proposed. For example, the thermoplastic polyimide adhesive currently indicated by USP4,543,295 is known. However, such polyimide pasted up substrates, such as copper or a polyimide film, and since it needed the thermo-compression-bonding temperature of not less than 250 ** in order to obtain satisfying adhesive strength, it had a difficulty in respect of practicality.
[0006]In order to perform thermo compression bonding at low temperature, the adhesives

using the polyimide which uses a diaminopolysiloxane and aromatic tetracarboxylic acid as a raw material are proposed (JP,4-23879,A). However, in such a polyimide simple substance, there was a fault that adhesive strength was not enough and was inferior to reliability.

[0007]As polyimide system adhesives excellent in adhesive strength, the film adhesive which becomes JP,52-91082,A from polyamidoimide and an epoxy resin as adhesives for manufacture of the copper-clad film for flexible printed wiring boards is indicated. However, when it uses for adhesion of the rugged surfaces in which circuits, such as multilayer printed wiring board manufacture, were formed, such a film does not have the enough restoration nature to a circuit face, and cannot fully obtain heat resistance to a solder bath.

[0008]For this reason, as the adhesives for multilayer PURINDO boards, and adhesives for cover lay films, low-temperature sticking by pressure of 250 ** or less is possible, and the material which was moreover excellent in adhesive strength, chemical resistance, heat resistance, moisture absorption solder heat resistance, the dimensional stability at the time of wiring processing, etc. has come to be called for.

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EFFECT OF THE INVENTION

[Effect of the Invention]Compared with the conventional polyimide system adhesives, thermo compression bonding of the heat-resistant binder film for printed circuit boards of this invention at low temperature is attained, without spoiling the original outstanding heat resistance of polyimide, and an electrical property. Therefore, the heat-resistant binder film for printed circuit boards by this invention can be used conveniently for the adhesives for multilayer printed boards, the adhesives for compound circuit boards, the adhesives for cover lay films, etc.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]This inventions are thermo-compression-bonding conditions 250 ** or less, and an object of this inventions is to provide the heat-resistant adhesive film for printed circuit boards excellent in heat resistance, moisture absorption solder heat resistance, processability, etc.

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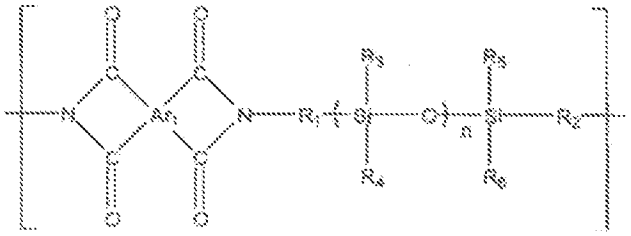
MEANS

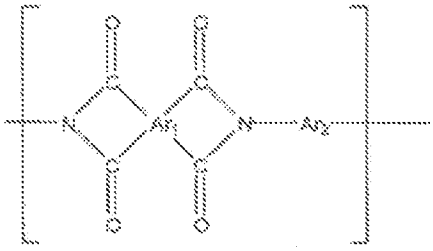
[Means for Solving the Problem]Namely, a solution which dissolved this invention in an organic solvent of a constituent which consists of 70 to 99 % of the weight of polyimide resin and 1 to 30 % of the weight of epoxy resins which have a silicon unit, After the surface coats on a substrate by which exfoliation processing was carried out, it is a manufacturing method of a heat-resistant adhesive film for printed circuit boards to dry. What consists of 70 to 99 % of the weight of polyimide resin which has a silicon unit, 1 to 30 % of the weight of epoxy resins, and 1 to 15 % of the weight of epoxy resin hardeners as said heat-resistant adhesive film for printed circuit boards is mentioned.
[0011]If mixing with polyimide resin is possible for an epoxy resin used in this invention, limitation in particular will not be carried out, but a weight per epoxy equivalent is a liquefied or powdered epoxy resin which is 500 or less range preferably. If a weight per epoxy equivalent exceeds 500, adhesive strength and heat resistance will fall. As an example of such an epoxy resin, bisphenol A, the bisphenol F. Phenols, such as the bisphenol S, a fluorene bisphenol, 4,4'-biphenol, 2,2'-biphenol, hydroquinone, and resorcinol, Or tris-(4-hydroxyphenyl) methane, 1,1,2,2-tetrakis (4-hydroxyphenyl) ethane, There is a glycidyl ether ghost derived from halogenated bisphenols, such as phenols more than trivalent [, such as phenol novolac and o-cresolnovolak,] or tetrabromobisphenol A. These epoxy resins can mix and use one sort or two sorts or more.
[0012]In this invention, it is desirable for a film moldability to use good solvent solubility polyimide as polyimide resin which has a silicon unit. As an example suitably used as polyimide which has solvent solubility, it is a following general formula (1).
[Formula 1]



(1)

(However, Ar_1 showing a tetravalent aromatic group, R_1 and R_2 showing a divalent hydrocarbon group, R_3 - R_6 showing the hydrocarbon group of the carbon number 1 - 6 values, and n showing the integer of 1-20), and a following general formula (2)

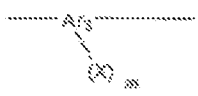
[Formula 2]



(2)

At least 1-mol % is a following general formula (3) among Ar2 [in / preferably / it has a repeating unit expressed with (however, Ar_1 shows a tetravalent aromatic group and Ar_2 shows a divalent aromatic group), and / the above-mentioned general formula (2)].

[Formula 3]



(3)

It is polyimide resin which has an aromatic group expressed with (however, Ar_3 shows a trivalent or tetravalent aromatic group, X shows a hydroxyl group, an amino group, or a carboxyl group, and m shows 1 or 2).

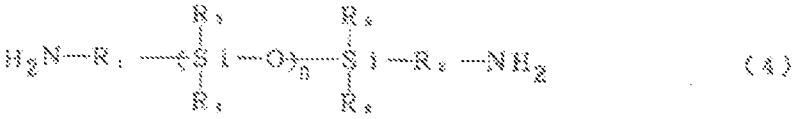
[0013]The polyimide resin which has a repeating unit expressed with the above-mentioned general formula (1) and (2) is obtained by making a diamino siloxane and aromatic diamine, and tetracarboxylic dianhydride react.

[0014]As an example of tetracarboxylic dianhydride, preferably 3,3',4,4'-diphenyl ether tetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and 2,2',2,3'-benzophenone tetracarboxylic dianhydride are mentioned. Otherwise, as a part of tetracarboxylic dianhydride ingredient, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 2,3,3',4'-biphenyl tetracarboxylic dianhydride,

pyromellitic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 3,4,9,10-perylene tetracarboxylic dianhydride, 3,3,6,7-anthracene tetracarboxylic dianhydride, 1,2,7,8-phenanthrene tetracarboxylic dianhydride, 4,4'-(hexafluoro iso PIRIDEN) phthalic acid dianhydride, etc. can also be used together.

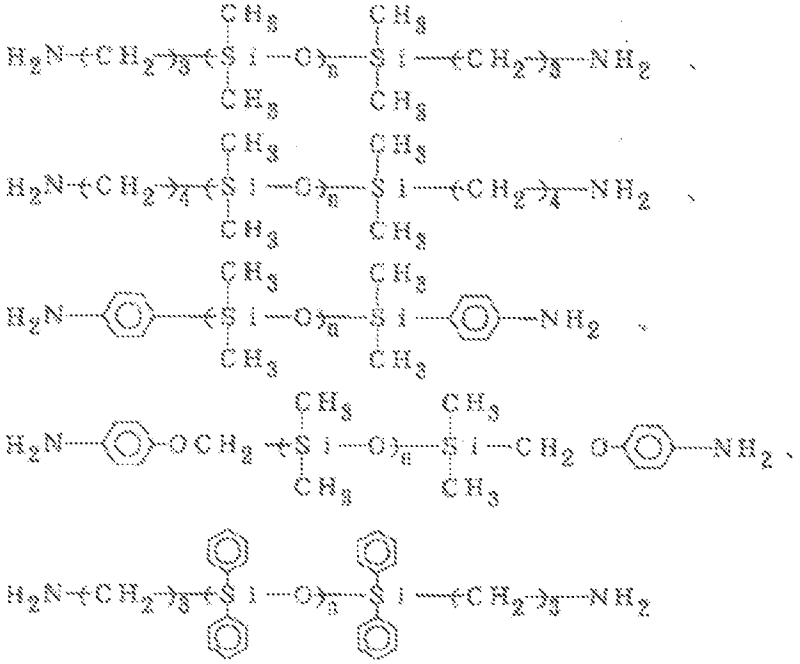
[0015]As a diamino siloxane, it is a following general formula (4).

[Formula 4]



(4)

The diamino siloxane expressed with (however, R_1 and R_2 show a divalent hydrocarbon group, R_3 - R_6 show the hydrocarbon group of the carbon numbers 1-6, and n shows the integer of 1-20) is used. As an example, it is preferably. [Formula 5]



** is mentioned. It is the range of 1-20 preferably [n / an average of / of these diamino siloxanes / more than], and is the range of 5-15 more preferably. Since the restoration nature of a heat-resistant adhesive film will fall if less than this range, it is not desirable. Since an adhesive property will fall if more than this range, it is not desirable. By introducing a silicon unit into polyimide resin using these diamino siloxanes, the mobility at the time of heat crimping can be given to the heat-resistant adhesive film of this invention, and the restoration nature to a plated printed circuit side can be raised.

[0016]As an example of aromatic diamine, m-phenylenediamine, P-phenylene diamine, 4,4'-diaminodiphenylpropane, A 4,4'-diaminodiphenylmethane, benzidine, 4, and 4'-diamino diphenyl sulfide, Although 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-

diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 4,4'-diamino-p-terphenyl, etc. are mentioned. In order to raise fusibility over an organic solvent 2,2-bis(3-aminophenoxy phenyl) propane, 2,2-bis(4-aminophenoxy phenyl)propane, a 3,3-bis(3-aminophenoxy phenyl)sulfone, A 4,4-bis(3-aminophenoxy phenyl)sulfone, a 3,3-bis(4-aminophenoxy phenyl)sulfone, A 4,4-bis (4-aminophenoxy phenyl)sulfone, 2,2-bis(3-aminophenoxy phenyl)hexafluoropropane, 2,2-bis (4-aminophenoxy phenyl)hexafluoropropane, 1,4-bis(4-aminophenoxy)benzene, It is preferred to use diamine which has three or more aromatic rings, 1,3-bis(4-aminophenoxy)benzene, 4,4-(p-phenylenedilsopropylidene) screw aniline, 4,4-(m-phenylenedilsopropylidene) screw aniline, etc.

[0017]It is more preferred to blend diamine which has an aromatic group expressed with the above-mentioned general formula (3) which has an epoxy resin and a functional group which has reactivity in a part of above-mentioned aromatic diamine. As aromatic diamine which has a reactive functional group to such an epoxy resin, 2,5-diaminophenol, 3,5-diaminophenol, 4,4'-(3,3'-dihydroxy) diaminobiphenyl, 4,4'-(2,2'-dihydroxy) diaminobiphenyl, 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, Although 3,3',4,4'-biphenyltetramine, 3,3',4,4'-tetraminodiphenyl ether, 4,4'-(3,3'-dicarboxy) diphenylamine, and 3,3'-dicarboxy-4,4'-diaminodiphenyl ether etc. are mentioned, They are 4,4'-(3,3'-dihydroxy) diphenylamine and 4,4'-(2,2'-dihydroxy) diphenylamine especially preferably. Since it reacts to an epoxy resin at the time of heat crimping and the structure of cross linkage is formed by using these aromatic diamine, adhesive strength of heat-resistant adhesives of this invention and chemical resistance can be raised further. aromatic diamine which has a reactive functional group to the above-mentioned epoxy resin -- all the aromatic diamine -- at least -- more than 1 mol % -- using is 1-10-mol% of the range desirable especially preferably.

[0018]Polyimide resin can manufacture polyimide resin which has a repeating unit expressed with said general formula (1) and (2) by [which made tetracarboxylic dianhydride react to the above-mentioned diamino siloxane and aromatic diamine in a solvent, and generated precursor resin] carrying out a back heating ring closure. It is preferred that ranges of percentage of a repeating unit expressed with the general formula (1) and (2) at this time are (1)/(2) =50 / 50 - 10/90. An effect of this invention is not acquired out of this range.

[0019]A blending ratio of polyimide resin and an epoxy resin which have the above-mentioned silicon unit is the range of 70 to 99 % of the weight of polyimide resin, and 1 to 30 % of the weight of epoxy resins. Heat resistance and an adhesive property can be raised further, without reducing the original characteristic of polyimide resin by blending in this range.

[0020]An epoxy resin hardener can also be blended with everything but the above-mentioned polyimide resin and an epoxy resin for the purpose of promotion of hardening as occasion demands. As an example of an epoxy resin hardener, acid anhydrides, such as amines, such as phenols, such as phenol novolac, o-cresolnovolak, and phenol resol, and

diethylenetriamine, pyromellitic dianhydride, and phthalic anhydride, are mentioned.
[0021]As for a blending ratio of each ingredient at the time of blending an epoxy resin hardener, it is preferred that it is the range of 70 to 98 % of the weight of polyimide resin, 1 to 15 % of the weight of epoxy resins, and 1 to 15 % of the weight of epoxy resin hardeners.
[0022]In this invention, a hardening accelerator more publicly known than before, a coupling agent, a bulking agent, paints, etc. other than each above-mentioned ingredient may be blended suitably if needed.
[0023]Although heat-resistant adhesives of this invention which consists of each above-mentioned ingredient are fabricated and used for film state, it is possible to film-ize using a publicly known method conventionally. As an example of a suitable forming process, resin which consists of an ingredient of polyimide resin, an epoxy resin, and others is dissolved in a solvent, It can be considered as a heat-resistant adhesive film for printed circuit boards of this invention by drying and exfoliating from a substrate, after the surface coats an obtained resin solution by a publicly known method conventionally on substrates, such as a metallic foil by which exfoliation processing was carried out, polyester film, and a polyimide film.
[0024]As a thing typical as a solvent used by the above-mentioned film forming cycle, N,N-dimethylformamide, a N,N-diethylformamide, N,N-dimethylacetamide, A N,N-diethylacetamide, a N,N-dimethyl methoxy acetamide, Amide system solvents, such as dimethyl sulfoxide and N-methyl-2-pyrrolidone, A tetrahydrofuran, diethylene glycol dimethyl ether, diethylene-glycol diethylether, Dioxane, gamma-butyrolactone, a xylenol, chlorophenol, Ether, such as phenol, methyl cellosolve, ethylcellosolve, methyl-cellosolve acetate, ethylcellosolve acetate, toluene, xylene, and methyl ethyl ketone, ester, and alcoholic solvent can be mentioned. Even if it uses a solvent used at the time of said polyimide resin manufacture as it is as a solvent at the time of film shaping, it does not interfere at all.
[0025]As the suitable directions for a heat-resistant adhesive film of this invention, For example, among bonded objects, such as a flexible printed circuit board, a glass fiber-epoxy wiring board, a paper-phenol wiring board, metal, and a resin base material, Insert a heat-resistant adhesive film of this invention, and it bonds by thermo-compression on condition of temperature of 20-250 **, the pressure 1 - 100 kg/cm^2, A method of making a glue line form between bonded objects is mentioned by carrying out predetermined time heat treatment at temperature of further 50-250 ** preferably, and stiffening an epoxy resin thoroughly.
[0026]
[Embodiment of the Invention]Since the polyimide which has a silicon unit used for the film for printed circuit boards of this invention is solvent solubility, while composite-izing with an epoxy resin is possible for it, since it has a silicon unit, mobility good at the time of thermo compression bonding is shown, and it has restoration nature and adhesion outstanding to the bonded object. By using the aromatic diamine which has an epoxy resin and reactivity, a

bridge is constructed with an epoxy resin and it has the feature that the glue line excellent also in intensity and heat resistance can be formed. Since the glass transition point is low, compared with the conventional polyimide system adhesives, it can paste up at low temperature far.

[Translation done.]

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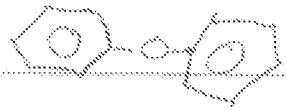

EXAMPLE

[Example]An example is shown below and this invention is explained to it in more detail. The cable address used by this example shows the following compounds.
ODPA:3,3',4,4'-diphenyl ether tetracarboxylic dianhydride DSDA:3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride BTDA:3,3',4,4'-benzophenone tetracarboxylic dianhydride BPDA :. 3,3',4,4'-biphenyl tetracarboxylic dianhydride BAPP:2,2'-bis(4-aminophenoxy phenyl)propane BAPS:bis(4-aminophenoxy phenyl)sulfone mBAPS : Bis(3-aminophenoxy phenyl)sulfone BisAM:. A 1,3-screw. (Aminoisopropyl) Benzene DABP:. 3,3'-diaminobenzophenone HAB:4, 4'-. (3,3'-dihydroxy) Diaminobiphenyl oDAP:. A 2,5-diaminophenol HFP:2,2'-screw. diamino Siloxane PSX-D: (3-amino-4 hydroxyphenyl) hexafluoropropane PSX-A: -- diamino siloxane PSX-B: of the average molecular weight 740 -- diamino siloxane PSX-C: of the average molecular weight 1000 -- the average molecular weight 1240. The diamino siloxane DGEBA of the average molecular weight 2000 : Bisphenol type A epoxy resin oCNB:o-cresolnovolak. Mold Epoxy-resin BCNB: Bromo cresol novolak type epoxy resin PNB: Phenol novolak resin
[0028]To the separable flask of 11 l. of examples, ODPA37.14g (0.11 mol), 200g of N-methyl-2-pyrrolidone and the diethylene glycol dimethyl ether 200g are inserted in, At a room temperature, use a dropping funnel for the well mixed next, and PSX-A 31.56g (n = 8.4 or 0.04 mol) is dropped at it, It ice-cooled under stirring of this reaction solution, o-DAP 1.52g (0.01 mol), BAPP30.25g (0.07 mol), and HAB1.04g (0.005 mol) were added, it stirred at the room temperature for 2 hours, and the polyamic acid solution was obtained. Temperature up was carried out to 190 **, it heated, this polyamic acid solution was stirred for 20 hours, and the polyimide solution of logarithmic viscosity 0.9 dl/g was obtained.
[0029]Next, mixed bisphenol A type epoxy resin (product [made from Oil recovery Shell Epoxy], Epicoat 828) 25 weight section, it was made to stir at a room temperature to solid content 75 weight section of the obtained polyimide solution for 2 hours, and the adhesive resin solution was prepared. This resin solution was applied on the glass plate, and it dried,

and it film-ized and was considered as the heat-resistant adhesive film. The 5% weight loss temperature under 120 ** and a nitrogen atmosphere was 450 ** the glass transition point of this film. Tensile strength, specific inductive capacity, and volume resistance were measured based on JIS C2330, respectively about this film. A result is shown in Table 2.

[0030]thus, the obtained heat-resistant adhesive film ~ the polyimide film (the Kaneka CORP. make.) of two sheets When it inserted between APIKARU and the sticking-by-pressure examination was done under the conditions of 25 kg/cm^2 for 200 ** and 60 minutes, the adhesive strength by a 180-degree peel test was 2.6 kg/cm. It was 1.8 kg/cm, when it bonded by thermo-compression on ****** and the same conditions between the oxidized copper foil of two sheets similarly and the adhesive strength by a 180-degree peel test was measured. After pasting up copper foil and being immersed for 30 seconds during a 300 ** solder bath, the adhesion state was observed, but it swelled, and defects, such as peeling, were not observed but showed good solder heat resistance.

[0031]The film was prepared by the presentation shown in Table 1 like Example 1 with the presentation shown in the two to example 10 table 1, and the various characteristics were measured. A result is shown in Table 2.

[0032]The film was prepared by the presentation shown in Table 1 like one to comparative example 5 example, and the various characteristics were measured. A result is shown in Table 2.

[0033]

[Table 1]

		ポリイミド樹脂（重量%）				エポキシ樹脂(wt%)	ゴム状樹脂変性量(wt%)
		芳香族ジアミン（モル）			芳香族ジアミン（モル）		
		芳香族ジアミン（モル）			シロキサンジアミン（モル）		
実施例	1	75				DGEBA 25	—
		ODPA 0.11	BAPP 0.07	HAB 0.005	PSX-A0 035		
	2	80				αCNB 20	—
		ODPA 0.11	BAPP 0.07	HAB 0.005	PSX-A0 035		
	3	80				αCNB 20	—
		ODPA 0.11	BAPS 0.06	HAB 0.005	PSX-B0 047		
	4	70				αCNB 20	PNB 10
		DSDA 0.12	BAPP 0.07	HAB 0.004	PSX-A0 036		
	5	80				BCNB 20	—
		DSDA 0.11	BAPS 0.06	pDAPS 0.03	PSX-C0 045		
	6	80				BCNB 20	—
		DSDA 0.13	mBAPS 0.06	HFP 0.004	PSX-D0 046		
	7	80				αCNB 20	—
		DSDA 0.1	BisAM 0.07	HAB 0.005	PSX-A0 035		
	8	75				αCNB 25	—
		BPDA 0.11	BisAM 0.07	HAB 0.005	PSX-A0 035		
	9	75				DGEBA 25	—
		BTDA 0.12	mBAPS 0.06	HAB 0.005	PSX-A0 035		
	10	70				αCNB 20	PNB 10
		ODPA 0.11	BAPP 0.07	HAB 0.005	PSX-A0 035		
比較例	1	100				—	—
		BTDA 0.10	DABP 0.10	—	—		
	2	100				—	—
		ODPA 0.11	BAPP 0.07	—	PSX-A0 040		
	3	95				DGEBA 5	—
		ODPA 0.11	BAPP 0.06	—	PSX-A0 050		
	4	100				—	—
		DSDA 0.11	BAPP 0.10	HAB 0.01	—		
	5	85				DGEBA 5	—
		DSDA 0.11	BAPP 0.10	HAB 0.01	—		

[0034]

[Table 2]

	ガラス転移温度	熱分解温度	引張強度	比誘電率	体積抵抗率	接着強度 1	接着強度 2	接着強度 3	はんだ耐熱性 1	はんだ耐熱性 2
実施例	(℃)	(℃)	kg/cm²		x10¹⁷ Ω cm	kg/cm²			(℃)	
1	120	350	7.2	3.1	2	1.8	1.2	2.8	>300	300
2	125	410	7.4	2.9	3	1.5	1.0	2.4	>300	300
3	145	430	6.0	3.0	2	1.8	1.2	2.2	>300	300
4	140	445	7.6	2.9	3	1.8	1.1	2.6	>300	300
5	165	410	6.8	3.0	2	1.9	1.3	2.8	>300	230
6	170	420	5.7	3.1	2	1.8	1.2	2.4	>300	300
7	130	410	7.3	3.0	2	1.6	1.2	2.2	>300	300
8	150	430	7.1	3.0	2	1.5	1.1	2.0	>300	280
9	155	450	6.7	3.1	2	1.6	1.1	2.0	>300	290
10	145	435	7.0	3.2	2	1.9	1.3	2.6	>300	300
比較例										
1	200	330	18.0	3.4	2	0.4	0.1	0.3	260	240
2	130	460	7.5	3.0	1	0.5	0.1	0.3	270	250
3	140	450	8.1	3.1	2	0.7	0.3	0.4	260	240
4	170	470	13.5	3.2	2	0.6	0.1	0.4	240	220
5	165	440	13.0	3.2	2	1.7	0.1	0.5	250	230

[0035]In Table 2, the adhesive strength 1 is the 180-degree peel strength to oxidation treatment copper, the adhesive strength 2 is the 180-degree peel strength to vitriolization copper, and the adhesive strength 3 is the 180-degree peel strength to a polyimide film. The solder heat resistance 1 is an inspection about a blister, peeling, and appearance after 30-

second immersion at a solder bath, and the solder heat resistance 2 inspects a blister, peeling, and appearance after 30-second immersion to a solder bath after 40 **, 90%RH, and 24-hour moisture absorption.

[0036]2 sets of flexible printed circuit boards by which the circuit was formed in both sides of example 11 polyimide film with copper are prepared, After inserting the heat-resistant adhesive film obtained in Example 1 in the meantime and bonding by thermo-compression on condition of for the temperature of 200 **, pressure 25 kg/cm^2, and 60 minutes, the through hole was formed and the multilayer printed wiring board was manufactured. There is also no generating of a smear etc. in the case of through hole formation, and the good through hole was obtained. Although this multilayer printed wiring board was immersed in a 300 ** solder bath for 30 seconds, it swelled and defects, such as peeling, were not observed.

[0037]The multilayer printed wiring board was manufactured like example 12 Example 8 using the heat-resistant adhesive film obtained in Example 10. There is also no generating of a smear etc. in the case of through hole formation, and the good through hole was obtained. Although this multilayer printed wiring board was immersed in a 300 ** solder bath for 30 seconds, it swelled and defects, such as peeling, were not observed.

[Translation done.]